ARMY RESEARCH LABORATORY

High Tc Superconductivity in the Triple-Perovskite La-Rare Earth or Alkali Metal-Ba-Ca-Mg or Cd-Cu-Oxide System

Arthur Tauber, Steven C. Tidrow, Daniel Pierce
and Donald W. Eckart

ARL-TR-1131 March 1997

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

NOTICES

Disclaimers

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
March 1997

3. REPORT TYPE AND DATES COVERED
Technical Report: Jan 96 to Dec 96

4. TITLE AND SUBTITLE
High T_c Superconductivity In The Triple-Perovskite La-Rare Earth or Alkali Metal-Ba-Ca-Mg or Cd-Cu-Oxide System

5. FUNDING NUMBERS
PR: 611102
PE: H94

6. AUTHOR(S)
Arthur Tauber*, Steven C. Tidrow, Daniel Pierce, and Donald W. Eckart

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army Research Laboratory (ARL)
Sensors and Electron Devices Directorate (SEDD)
ATTN: AMSRL-SE-EI
Fort Monmouth. NJ 07703-5601

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1131

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*Arthur Tauber is with Geo-Centers, Inc., 615 Hope Road, Eatontown, NJ 07703.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Bulk targets of compounds in the system $La_{3-z}Me_zBa_3Ca_{1-v}Nc_vCu_7O_{16+v}$ where Me=rare earth or Na and Nc=Mg or Cd were prepared by solid state reactions. They were employed to deposit by pulse laser deposition thin films of the superconductor on single crystal substrates of $LaAlO_3$, LSAT, and GGG. Phase relationships and orientation relationships were obtained from diffractometer scans. All compounds exhibited a (00ℓ) relationship with all substrates. Lattice parameters, transition temperatures and widths are reported for each superconducting compound. All substituted compounds were superconducting but no increase in Tc was observed for any. All thin films heated to 750 deg C desorbed little oxygen compared to YBCO.

14. SUBJECT TERMS
High temperature superconductivity; thin films; perovskite; oxygen transition temperature

15. NUMBER OF PAGES
10

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

CONTENTS

TABLE

FIGURE

HIGH T_c SUPERCONDUCTIVITY IN THE TRIPLE-PEROVSKITE La-RARE EARTH OR ALKALI METAL-Ba-Ca-Mg OR Cd-Cu-Oxide SYSTEM

INTRODUCTION

The high T_c superconducting system $La_{3-z}Me_zBa_3Ca_{1-v}Nc_vCu_7O_{16+x}$ is attractive for device applications because it is stable with regard to oxygen compared to $YBa_2Cu_3O_{6+x}$ and undergoes no phase transition between the sintering temperature and room temperature [1]. Thermal cycling demonstrated reversible oxygen losses of less than 1% up to 1000 °C in bulk samples [2]. One useful consequence should be more easily prepared multilayered structures and such multilayered devices as Josephson junctions, broadband impedance transformers, and flux flow and field effect transistors. One objective of this investigation has been the preparation and characterization of thin films of $La_3Ba_3CaCu_7O_{16+x}$. A second objective has been an investigation of the effect of substitutions for La and Ca with the hope of increasing T_c.

A superconducting bulk compound in the system $La_{3-z}Me_zBa_3Ca_{1-v}Nc_vCu_7O_{16+x}$ where z=0 and v=0, namely $La_3Ba_3CaCu_7O_{16+x}$ (La3317), was first prepared by Engelsberg [3]. The material was found to be a superconductor with a T_c= 80.2 K and to have a triple perovskite structure. It is tetragonal with $c=3a$ (c=11.61, a=3.87). In an earlier study [4], carried out on a composition close to La3317, it was deduced that most of the Ca atoms occupy the central position of the unit cell that is occupied by Y atoms in $YBa_2Cu_3O_{6+x}$ (YBCO). Recently Kao et al. [5] reported that about half of the Ca enter the Y sites and the remainder are on Ba sites. Similar results have been obtained in studies of other La-Ba-Ca-Cu-oxides [4,6] where much of the La is found on the Ba sites.

The substitution of Mg and Sc for Ca was already investigated by Engelsberg [3]. He found a slight increase in lattice parameter when Mg is substituted, c=11.71Å and a=3.91Å; and superconductivity was observed below 30 K. Sc substitution led to a multiphase material and no superconductivity was observed. Wu et al. [7] have investigated rare earth substitution for La in bulk samples.

EXPERIMENT

Bulk samples and targets, in the system $La_{3-z}Me_zBa_3Ca_{1-v}Nc_vCu_7O_{16+x}$ where Me=Nd, Yb, Y and Nc=Mg or Cd, were prepared for pulsed laser deposition (PLD) by mixing precursor powders of La_2O_3, Nd_2O_3, Yb_2O_3, Y_2O_3, Na_2CO_3, MgO, and $CdCO_3$ in a BC mortar until homogeneous. The powder was pressed into 2.54 cm discs and heated in air at 3 °C/min to 975 °C and held for 10 hours, cooled at 3 °C/min and removed from the furnace. Subsequently, the disc was reground to a powder of <100 μm particle size and pressed into 2.54 cm diameter discs and re-pressed isostatically at 344 MPa. The discs were then heated at 3 °C/min to 1000 °C, held for 24 hours, in flowing oxygen gas. Lattice parameters were obtained from powder diffractometer scans taken between 15-155° 2θ using CuKα radiation (λ=1.54056 Å). Lattice parameters are reported in Table 1. Thin films prepared by PLD averaged about 300 nm thick. The observed reflections from films obtained by θ–2θ scans are reported in Table 1. Deposition parameters are as follows: KrF excimer laser (λ=248 nm) was used at a pulse repetition rate of 10 Hz and a laser fluence of 1-2 J/cm^2 at the target. The chamber was maintained at an oxygen pressure of 13.6 Pa and the heater block holding the substrates was held at 850 °C. Deposition times were about 10 minutes. Samples were cooled rapidly to 650 °C and then to 400°C in 5.17 kP of oxygen in 1/2 hr. The substrates employed in this investigation were single

crystal (211) GGG, (100) $LaAlO_3$, and (100) LSAT (a solid solution of 30 mole % $LaAlO_3$-70 mole % Sr_2AlTaO_6) [8,9]. The superconducting transition temperature and transition width were measured using an ac Eddy current apparatus. Bulk or thin film samples were mounted on a sapphire block in which a detecting pick up coil has been imbedded. The sample is mounted on the sapphire block above the detecting coil. An exciting coil driven at 100 MHz is placed above the sample. The sapphire block is in contact with the thermal sink of a closed cycle helium cryostat.

TABLE 1. Properties of $La_{3-z}Me_zBa_3Ca_{1-v}Cu_7O_{16+x}$ Compounds.

Compound	Lattice Parameter (Å)		Onset T_c (K)	ΔT_c (K)	Observed Reflections
	c	*a*			
$La_3Ba_3CaCu_7O_{16+x}$	11.650 11.680*	3.865	72 80*	4	
$La_3Ba_3CaCu_7O_{16+x}$/LSAT	11.665				003,005,006,007,0012
$La_3Ba_3CaCu_7O_{16+x}$/GGG	11.540				003,005,006,007,009
$La_3Ba_3CaCu_7O_{16+x}/LaAlO_3$	11.660		35	15	003,004,005,006,007, 009,0011,0012
$La_2YBa_3CaCu_7O_{16+x}$	11.580	3.850	72	3	
$LaY_2Ba_3CaCu_7O_{16+x}$	11.630	3.868	74	6	
$LaY_2Ba_3CaCu_7O_{16+x}$/LSAT	11.703				002,005,006,007
$Nd_3Ba_3CaCu_7O_{16+x}$	11.614	3.874	42		
$Nd_3Ba_3CaCu_7O_{16+x}$/LSAT			40	20	
$La_2YbBa_3CaCu_7O_{16+x}$	11.530	3.843	74	5	
$La_2YbBa_3CaCu_7O_{16+x}$/LSAT	11.628		45	>20	003,005,006,007, 009,0010,0011
$La_2YbBa_3CaCu_7O_{16+x}/LaAlO_3$	11.630				003,005,006,007,008, 009,0010,0011
$La_2YbBa_3CaCu_7O_{16+x}$/GGG	11.683				003,005,006,007
$La_{2.5}Na_{.5}Ba_3CaCu_7O_{16+x}$	11.630	3.870	68	18	[multiphase]
$La_{2.5}Na_{.5}Ba_3CaCu_7O_{16+x}/LaAlO_3$	11.662		65	>40	003,005,006,007
$La_{2.5}Na_{.5}Ba_3CaCu_7O_{16+x}$/GGG	11.664				006,009
$La_3Ba_3Ca_{.5}Cd_{.5}Cu_7O_{16+x}$	11.661	3.881	55		
$La_3Ba_3Ca_{.5}Cd_{.5}Cu_7O_{16+x}$/LSAT	11.720				003,006
$La_3Ba_3Ca_{.5}Cd_{.5}Cu_7O_{16+x}/LaAlO_3$	11.265		70	>45	003,006
$La_3Ba_3Ca_{.5}Cd_{.5}Cu_7O_{16+x}$/GGG	11.730				003,006,007
$La_3Ba_3Ca_{.5}Mg_{.5}Cu_7O_{16+x}$	11.661	3.890	35	15	
$La_3Ba_3Ca_{.5}Mg_{.5}Cu_7O_{16+x}/LaAlO_3$	11.650				003,005,006,007, 009,0010,0011
$La_3Ba_3Ca_{.5}Mg_{.5}Cu_7O_{16+x}$/GGG	11.692				003,005,006,007,0011

*Reference [3].

Desorption of oxygen from several films was investigated as a function of temperature using thermal desorption mass spectrometry. This involves detecting desorbing O_2 using a double focusing mass spectrometer. The spectrometer has high mass resolution which allows the oxygen signal to be separated from other interfering species such as hydrocarbons of the same nominal mass (i.e., 32 AMU). For analysis, a piece of a thin film coated substrate was introduced into a tantalum foil cell. Spotwelded to the cell was a 0.005 in. 5%Re-W/26%Re-W thermocouple. The cell was attached to a vacuum feedthrough that allowed samples to be moved into a roughing chamber and then into an analysis chamber containing the mass spectrometer. The base pressure of the analysis chamber at the onset of the desorption was in the mid 10^{-9} Torr range. This provided a low oxygen background and an increased sensitivity for detecting oxygen originating from the contents of the cell. The cell temperature could be ramped to 1500 °C, but typically a maximum of 800 °C was used. A linear temperature ramp of 1.4 K/sec was maintained using a feedback temperature controller and a 100 amp power supply. The area of the film was determined by computer processing a scanned image of the sample. The sample thickness was determined by fracturing a coated substrate and measuring the film cross section using scanning electron microscopy. The oxygen desorption spectra were then normalized to the calculated volume of the film for each sample respectively.

RESULTS

All substitutions for either La or Ca resulted in the preservation of the tetragonal structure. In bulk samples, changes in intensity of x-ray diffraction lines are consistent with the increase or decrease in the scattering power of the substituent. Very small changes in the *c* lattice parameter are also noted, consistent with the changes in ionic radii of substituent ions, while the *a* parameter exhibited a slight expansion. For thin films, contractions in the *c* parameter were observed when the substrate was $LaAlO_3$; slight expansion was found when LSAT or GGG substrates were used. The results of lattice expansion or contraction of the film are consistent with known lattice parameters for the substrates. All films showed the same epitaxial relationship regardless of substrate: $La_{3-z}Me_zBa_3Ca_{1-y}Nc_yCu_7O_{16+x}$ (00ℓ) on (100)$LaAlO_3$, on (100)LSAT or on (211) GGG, Table 1. The strongest reflection from each of these films was always (006). The best quality films obtained, as judged by the presence of higher order reflections, were those deposited on $LaAlO_3$. This may be due to the fact that of all the substrates employed, only $LaAlO_3$ placed the films in compression, or film deposition conditions were not optimized.

CONCLUSIONS

All substituent compounds exhibited high T_c superconductivity, although the transition temperatures were lower than in the unsubstituted compounds. The highest transition temperatures were obtained when rare earth ions replaced La. Engelsberg found that the substitution of Mg for Ca resulted in a reduced T_c [3]. We observed a T_c=35 K upon the replacement of half of the Ca by Mg; this was close to what Engelsberg observed. On the other hand, the substitution of half the Ca by Cd in this investigation resulted in a much higher transition temperature, 55 K. The fact that divalent Cd is much larger than Mg and has an ionic radius close to Ca suggests that ionic size might be a major factor influencing superconductivity. However, the nature of the bonding is probably a major factor as well.

All the thin film compounds prepared in this investigation desorb very little oxygen when heated compared with YBCO, Fig. 1(A). When some La is replaced by Na the largest desorption for any substituted compound was observed, Fig. 1(C). The substitution of Cd for Ca has a smaller effect, Fig. 1(E). It appears that occupancy by light rare earths (large ionic radii), in the rare earth site for this triple perovskite structure, strongly influences the retention of oxygen with heating.

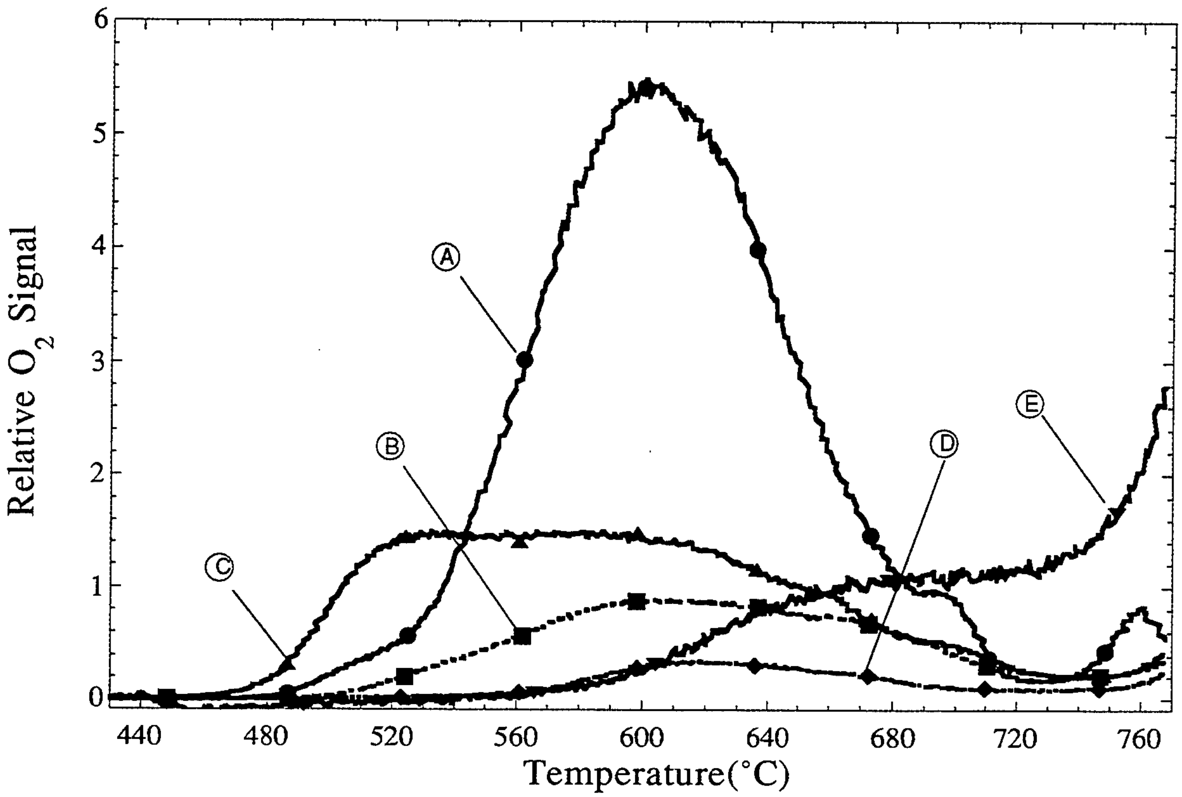

Figure 1. Desorption of oxygen from thin films: (A) $YBa_2Cu_3O_{6+x}$, (B) $Nd_3Ba_3CaCu_7O_{16+x}$, (C) $La_{2.5}Na_{.5}Ba_3CaCu_7O_{16+x}$, (D) $La_3Ba_3CaCu_7O_{16+x}$ and (E) $La_3Ba_3Ca_{.5}Cd_{.5}O_{16+x}$.

REFERENCES

1. D.S. Wu, H.-C.I. Kao, M.K. Wu and C.M. Wang, Physica C, **214**, 261 (1993).
2. M. Nicolas, B. Mettout and K. Sauv, Physica C, **249**, 377 (1995).
3. S. Engelsberg, Physica C, **176**, 451 (1991).
4. H. Fujishita, S. Shamoto, M. Onoda and M. Sato, Jpn. J. Appl. Phys., **28**, 754 (1989).
5. H.C. Kao, Y.D. Leu, W.N. Haug, C.M. Wang, D.H. Chen and T.J. Lee, Supercond. Sci. Technol., **9**, 1 (1996).
6. C.M. Wang, Y.F. Yang, H.-C.I. Kao and W.C.J. Wei, J. Chin. Chem. Soc., **39**, 67 (1992).
7. D.S. Wu, Y.F. Yang, H.-C.I. Kao and C.M. Wang, Physica C, **212**, 32 (1996).
8. C.D. Brandle, G.W. Berkstresser, V.J. Fratello and A.J. Valentino, 9th American Conference on Crystal Growth, Baltimore, MD, 1-6 August 1993 (invited presentation).
9. S.C. Tidrow, A. Tauber, W.D. Wilber, R.T. Lareau, In Press, Proceedings of Applied Superconductivity Conference (1996).

ARMY RESEARCH LABORATORY
SENSORS AND ELECTRON DEVICES DIRECTORATE
MANDATORY DISTRIBUTION LIST

Defense Technical Information Center*
ATTN: DTIC-OCC
8725 John J. Kingman Rd, STE 0944
Fort Belvoir, VA 22060-6218
(*Note: Two DTIC copies will be sent from STINFO office, Ft Monmouth, NJ)

Director
US Army Material Systems Analysis Actv
ATTN: DRXSY-MP
(1) Aberdeen Proving Ground, MD 21005

Commander, AMC
ATTN: AMCDE-SC
5001 Eisenhower Ave.
(1) Alexandria, VA 22333-0001

Director
Army Research Laboratory
ATTN: AMSRL-D (John W. Lyons)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
ATTN: AMSRL-DD (COL Thomas A. Dunn)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197
(1) AMSRL-OP-SD-TA (ARL Records Mgt)
(1) AMSRL-OP-SD-TL (ARL Tech Library)
(1) AMSRL-OP-SD-TP (ARL Tech Publ Br)

Deputy Director
Army Research Laboratory
Sensors & Electron Devices Directorate
Fort Monmouth, NJ 07703-5601
(1) AMSRL-SE
(1) AMSRL-SE-C (V. Rosati)
(1) AMSRL-SE-C (M. Hayes)
(1) AMSRL-OP-FM-RM
(22) Originating Office

Advisory Group on Electron Devices
ATTN: Documents
Crystal Square 4
1745 Jefferson Davis Highway, Suite 500
(2) Arlington, VA 22202

Commander, CECOM
R&D Technical Library
Fort Monmouth, NJ 07703-5703
(1) AMSEL-IM-BM-I-L-R (Tech Library)
(3) AMSEL-IM-BM-I-L-R (STINFO Ofc)

Deputy for Science & Technology
Office, Asst Sec Army (R&D)
(1) Washington, DC 20310

HQDA (SARDA-TR)
Dr. Richard Chait
(1) Washington, DC 20310

Director
Naval Research Laboratory
ATTN: Code 2627
(1) Washington, DC 20375-5000

USAF Rome Laboratory
Technical Library, FL2810
ATTN: Documents Library
Corridor W, STE 262, RL/SUL
26 Electronics Parkway, Bldg 106
Griffiss Air Force Base
(1) NY 13441-4514

Dir, ARL Battlefield
Environment Directorate
ATTN: AMSRL-BE
White Sands Missile Range
(1) NM 88002-5501

Dir, ARL Sensors, Signatures,
Signal & Information Processing
Directorate (S3I)
ATTN: AMSRL-SS
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Dir, CECOM Night Vision/
Electronic Sensors Directorate
ATTN: AMSEL-RD-NV-D
(1) Fort Belvoir, VA 22060-5806

Dir, CECOM Intelligence and
Electronic Warfare Directorate
ATTN: AMSEL-RD-IEW-D
Vint Hill Farms Station
(1) Warrenton, VA 22186-5100

Cdr, Marine Corps Liaison Office
ATTN: AMSEL-LN-MC
(1) Fort Monmouth, NJ 07703-5033